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Limits of Inflammability and Energy of Activation*

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INTRODUCTION

The limiting condition for gaseous explosion or inflammation at high temperatures has been discussed principally from the viewpoint of the chain theory.[1)2)3)] In the chain theory, the condition for explosion or inflammation was defined as a condition at which the reaction rate in gaseous phase becomes infinitely high. This definition means that the gaseous explosive reaction proceeds homogeneously in the gaseous phase with the wall effect as chain breaker. However, it was shown by GOTO in 1942[4)5)] that inflammation in an oxy-hydrogen gas mixture does not occur simultaneously through the whole gaseous phase but starts at the nearest part to the wall of the reaction vessel heated at a high temperature.

This experiment suggests that inflammation of combustible gas mixture even in a heated vessel proceeds through at least two stages, *i. e.* local occurrence of a flame and its propagation through gaseous phase. It is obvious that process of inflammation is not homogeneous in the case of the spark ignition or ignition by heated wire. Thus, gaseous explosion may be generally understood as a process of flame occurrence and its propagation.

Now, explosive reaction or inflammation is characterized by the presence of limiting condition and its propagating property. When ignition takes place, the condition for propagation must necessarily be satisfied. And flame propagation may be regarded as a succesive occurrence of ignition. Accordingly, from the viewpoint of energetics, the limiting condition is expected to be derived from that for propagation. Among various kinds of limits, the limits of concentration are preferable to be discussed, for they give the most reliable values and they seem to be characteristic of combustibles.

In this review, limits of inflammability and activation energy are to be discussed in relaton to the kinetic energy of molecules concerned.

I. CONDITIONS FOR INFLAMMATION AND PROPAGATION

As is mentioned above, explosive reaction is essentially not homogeneous, but

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passes through the following two stages :

(a) Primary activation (or ignition) : generation of reactive zone (or a flame) by locally concentrated energy which may be given externally by an electric spark, surface reaction and so forth.

(b) Secondary activation : Propagation of the reactive zone which is self-supported by successive liberations of combustiosn heat in the flame front.

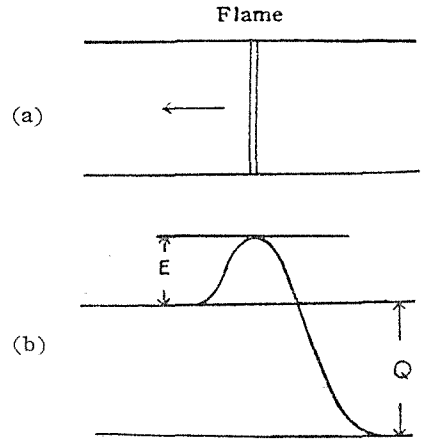


Fig. 1. Flame propagation and process of activation.

Regarding a flame front as an assemblage of activated molecules, flame propagation may correspond to an activation process as illustrated in Fig. 1 (a) and (b). In other words, the reactant molecules in the adjacent layer to the flame front are to be activated by the energy released at the flame front and estimated to be the sum of the reaction heat Q and the activation energy E.

Now, it is assumed fundamentally as follows :

(1) Every reactive zone of the flame front liberates the energy H (kcal/mole) with respect to the stoichiometric elementary reaction which should be given by the sum of the combustion heat Q and the activation energy E. A fraction of the energy H may be consumed for activation of adjacent zone.

(2) The energy liberated in the reaction zone must not be less than the energy given for activation in order to ignite the explosive mixtures or to propagate the flame reaction.

(3) Concerning the energy, the necessary condition for ignition coincides with that for propagation, at the limit of concentration.

Now, let n be the number of the stoichiometric elementary reaction in the unit volume of the flame front, then the energy to be liberated by the reaction is nH and the number of the elementary reactions to be induced with this energy may be represented by $\alpha nH/E$, where α is an efficiency coefficient of activation. Hence, the

energy to be liberated from the new reaction zone is to be $\alpha\, nH^2/E$. From the fundamental postulate (2), the condition for propagation is given by the relation,

$$(\alpha\, nH^2/E)/nH \geqq 1 \tag{1}$$

or

$$\alpha\, H/E \geqq 1\,. \tag{2}$$

As to the condition for initiating a flame or ignition, representing the primary activation energy by W and putting $nH=W$ in the equation (1), we obtain the same formula with the relation (2). Thus the relation (2) holds good of both ignition and propagation.

II. LOWER LIMITS AND HEAT OF COMBUSTION

Assuming that the efficiency coefficient α is proportional to the concentration, at the lower limit c_1 (volume fraction) the relation (2) becomes

$$k\, c_1\, H/E=1\,, \tag{3}$$

where k is a proportional constant. Since

$$H=Q+E \tag{4}$$

the equation (3) can be written in the form :

$$1/c_1=(k/E)Q+k\,. \tag{5}$$

Activation energy, E, for various combustibles are not necessarily to take the same values. Using data shown by G.W. Jones,[6] and plotting $1/c_1$ against Q, it was found

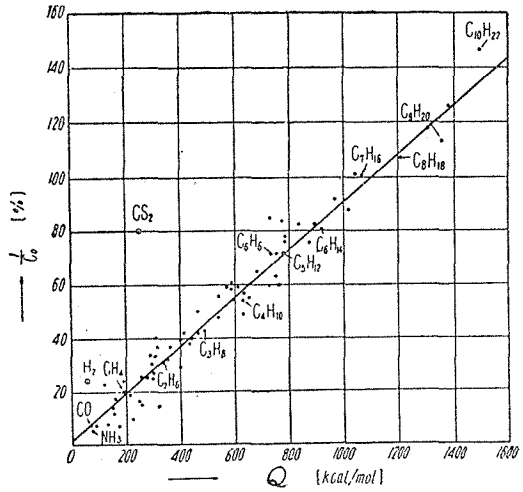


Fig. 2. Correlation between lower limit of inflamation and molar heat of combustion of fuels.

that nearly linear relation holds between them for most combustibles as shown in Fig. 2.* Recently, Egerton and Powling[7] showed slightly curved correlation between $\frac{1}{c_1}$ and Q for several hydrocarbons.

Fig. 2 and Equation (5) suggest that E is almost constant for most of combustibles. At least, the equation (5) applies to most combustibles as a semi-empirical formmla.

By the method of least squares, from Fig. 2 we have $k/E=0.090$ and $k=1.56$. Accordingly by approximate estimation we obtain, $E=17$kcal. The value of k is expected to have relatively wide fluctuation in comparison with the value of k/E. Accordingly, the estimation of E shown above gives only the order of magnitude.

Apparent constancy of the activation energy suggests that primary activation process may be similar with most combustibles and that the minimum ignition energy may be identical. Experimental results of Blanc, Guest, von Elbe and Lewis[9] with respect to spark ignition show the propriety of the above suggestion.

Neglecting k in Eq. (5),** we obtain an approximate relation as follows :

$$c_1 Q \cong E/k \cong 11 \text{ (kcal)} \qquad (6)$$

From the relation (6) the lower limit of combustibles at ordinary temperatures can be predicted, if the heat of combustion is known. Since the partial pressure of the combustibles at their lower limits under the atmospheric pressure can be calculated, the flashing points of them can also be predicted, if the vapor presssure-temperature relation is known. Table 1 shows some examples for various organic substances which are not included in Fig.2.

Table 1. Lower limits and flashing points of volatile organic compounds.

Combustible	Q (kcal/mole)	Flashing pts. °C		Lower Limits (%)	
		obs.	calc.	obs.	calc.
Naphthalene	1231.9	84	82	0.99	0.91
Tetraline	1352.4	77	78	0.78	0.89
Phthalic anhydride	783.8	149	146	1.55	1.44
Salicylic acid	723.1	140	146	1.04	1.50
Anthracene	1700.4	175	175	0.65	0.65
Camphor	1410.7	80	79	0.89	0.78
Borneol	1469.6	94	93	0.77	0.75
Anthraquinone	1544.5	218	220	0.65	0.71

* The lower limit varies considerably with the direction of propagation, especially in the case of gases with lower molecular weight. From theoretical standpoint, the limits for horizontal propagation may be preferable, if those values are available. Data of Jones give the lowest values for upward propagation for safety purposes. In this report, data of Jones have mainly been refered to and a marked deviation was shown for hydrogen and carbon disulfide. Corresponding horizontal values obtained by Bone and Townend[8]. come nearer to the straight line.

** If E can be neglected in comparison with Q in Eq. (4), the same relation with Eq. (6), may be derived.

Observed values in Table 1 have been obtained in our laboratory*. Table 2 shows fair agreement between calculated and observed values available for various fuels. Since the inflammation limlts of concentration are dependent on the temperature as will be mentioned later in this review, the calculated values must be corrected to some extent at higher temperatures.

Table 2. Flashing point and lower limits of organic liquids.

Combustible	Q (kcal)	Flash. Pts. (°C)		Lower Limits (%)	
		obs.	calc.	obs.	calc. $(11/Q)$
Benzene	782	-12 ~-10	-12	1.41	1.4
Toluene	934	6.5	5	1.27	1.2
Xylene	1090	23	23	1.00	1.0
n-Propyl benzene	1246	30.5	31	—	0.88
n-Hexane	990	-18	-27	1.25	1.1
n-Heptane	1150	-1 ~-17	-4	1.00	0.95
n-Octane	1303	17	13	0.95	0.84
Ethyl formate	392	-19.5	-22	2.75	2.8
Methyl acetate	381	-15.5	-18	3.15	2.9
Ethyl acetate	537	-5.0	-8	2.18	2.0
Phenol	732	79	75	—	1.5
o-Cresol	883	81 ~ 83	77	—	1.2
m-Cresol	881	86	87	—	1.2
p-Cresol	883	86	88	—	1.2
β-Naphtol	1187	161	145	—	0.92
Hydroquinone	684	165	166	—	1.6
Methanol	171	6.5	9	6.72	6.4
Ethanol	328	9	11	3.28	3.5
n-Propyl alcohol	481	22.5	23	2.55	2.3
n-Butyl alcohol	639	35	35	1.70	1.7
iso-Amyl alcohol	794	40 ~ 42	40	1.20	1.4
Benzyl alcohol	894	142	92	—	1.2
Diethylene glycol	566	124	139	—	1.9
Benzaldehyde	841	62.5	62	—	1.3
Acetone	427	-20	-21	2.55	2.6
Ethylene oxide	309	0	-52	3.00	3.6
Nitrobenzene	739	88 ~ 90	87	—	1.5
Aniline	812	71	70	—	1.4
Dimethyl aniline	1143	61 ~ 76	63~68	—	0.96
Benzoic acid	771	131	133	—	1.4
Carbon disulfide	247	-25.5	-25	(-25°C)	4.5

*Experimental procedure will be published on this Bulletin later.

III. THE TEMPERATURE COEFFICIENT OF THE LOWER LIMIT AND THE ACTIVATION ENERGY

At the lower limit of concentration c_1, a unit cell is defined as a volume per one molecule of combustible gases (Fig. 3).

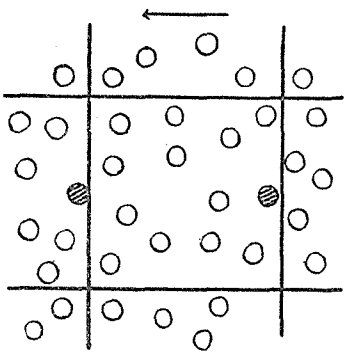
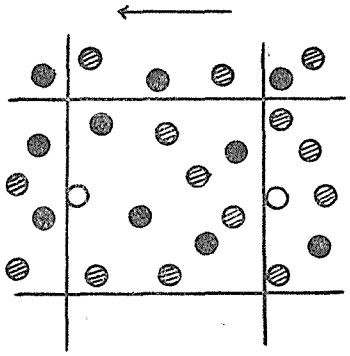


Fig. 3. (a) Unit cell for one molecule of combustible gas.

○ : Oxygen
◍ : Combustible molecules



(b) Unit cell for one molecule of oxygen.

○ : Oxygen
◍ : Combustible
● : Nitrogen

If in the unit cell at the lower limjt c_1, the number of excess molecules of supporter-gas (oxygen or air) per one molecule of combustibles is given by A, then

$$c_1=\frac{1}{1+A}\cong\frac{1}{A} \quad \text{or} \quad A\cong\frac{1}{c_1}\ . \tag{7}$$

Assuming that the energy H liberated in the reaction zone is given to the unit cell and distributed equally between all degrees of freedom of all the excess molecules in the cell as the kinetic energy, the energy parted to one molecule may be givin approximately by $(H/A+fRT/2)$ or $(c_1H+fRT/2)$,* where f is the degrees of freedom of the excess molecules, ($f=7$ for O_2 and N_2) and $RT/2$ is the kinetic energy per one degree of freedom of them at the absolute temperature of the experiment. If it is granted that ignition can occur or propagation proceeds when the energy of the excess molecules (principally oxygen) given above exceeds the activation energy E, then the condition for inflammation given by Equation (3) or (5) may be written in the forms

* The energy (ε) parted to every degree of freedom of excess molecules may be given by $(H/fA+RT/2)$.

$$c_1\ (Q+E)+fRT/2=f\varepsilon=E \tag{8}$$

or

$$\frac{1}{c_1}=\frac{Q}{E-fRT/2}+\frac{E}{E-fRT/2} \tag{9}$$

or

$$E=(c_1Q+fRT/2)/(1-c_1)^{*}\cong c_1Q+fRT/2 \tag{10}$$

or

$$c_1=E/Q-(fR/2Q)T. \tag{11}$$

Equation (9) is another expression of Eq. (5) ; Eq. (10) gives the value of activation energy E, and Eq. (11) gives the temperature coefficient of the lower limit c_1.

Table 3. Temperature coefficient of lower limits and activation energy.

Combustiblee	Q kcal/mole	Temp. Coeff. ($\times 105$)		E(kcal/mole) from Eq. (10)
		$\Delta C/\Delta T$ obs.	$fR/2Q$ calc.	
Hydrogen	58	$\left(\frac{0.034}{350}\right)$: 9.5	12	7.7(8.8% ; 100°C)
Carbon monoxide	68	$\left(\frac{0.030}{200}\right)$: 15	22	12.8(15% ; 100°C)
Ammonia	76	$\left(\frac{0.045}{400}\right)$: 11	9	15.9(17.5% ; 100°C)
Methane	196	$\left(\frac{0.002}{500}\right)$: 4.4	4	13.1(5.5% ; 100°C)
Pentane	775	$\left(\frac{0.0031}{283}\right)$: 1.1	0.9	13.8(1.58% ; 17°C)
Benzene	751	$\left(\frac{0.0024}{150}\right)$: 1.6	0.9	12.8(1.37% ; 100°C)
Toluene	892	$\left(\frac{0.0023}{100}\right)$: 2.3	0.8	13.8(1.26% ; 100°C)
Ethylene	311	$\left(\frac{0.0095}{383}\right)$: 2.5	2.3	12.7(3.45% ; 17°C)
Acetylene	302	$\left(\frac{0.0071}{283}\right)$: 2.3	2.3	10.6(2.90% ; 17°C)
Methanol	150	$\left(\frac{0.016}{200}\right)$: 8.0	4.7	13.4(7.5% ; 50°C)
Propyl alcohol	438	$\left(\frac{0.007}{150}\right)$: 4.7	1.6	13.4(2.45% ; 100°C)
Acetone	395	$\left(\frac{0.0008}{100}\right)$: 8.0	1.8	13.8(3.0% ; 25°C)

Mean value of $E=12.8$

Table 3 shows that the calculated values of the temperature coefficients of the lower limits at relatively low temperatures agree with the observed values in the order of magnitude. The activation energy calculated by Eq. (10) gives almost con-

* At the lower limit, $C_1 \gg 1$.

stant values for several kinds of gases, and agrees with the value (17 kcal) obtained from Fig. 2 and Eq. (5) in their order of magnitude. Observed values in Table 3 were taken from the data of U. S. Bureau of Mines[10].

In the preceding section, we have derived Eq. (5)

$$\frac{1}{c_1}=\frac{k}{E}Q+k \tag{5}$$

and from Fig. 2, we have odtained statistically,

$$\frac{k}{E}=0.090, \qquad k=1.56 \text{ and } E\cong 17 \text{ kcal.}$$

Camparing Eq. (5) with Eq. (9), we have

$$\frac{k}{E}=\frac{1}{E-fRT/2} \qquad \text{and} \qquad k=\frac{E}{E-fRT/2}. \tag{12}$$

Using the value of E (13 kcal) obtained from Table 3, k/E and k can be computed approximately as follows :

$$\frac{k}{E}=\frac{1}{E-fRT/2}=\frac{1}{13-2}=0.09, \qquad k=\frac{14}{11}=1.3$$

where $f=7$, $R=0.002$, and $T=300°K$.

Thus, we see the consistency between Eq. (5) and Eq. (8) or (9) though they have been derived in different ways. Further, the relation (12) gives the physical mean -ing of k. Since $E-fRT/2=c_1(Q+E)=H/A$ from Eq. (8), k is the ratio of activa -tion energy to the energy released and delivered to each molecule of oxygen in a unit cell. Since nitrogen and oxygen molecules have the same degrees of freedom, Eq. (8) holds approximately good both in oxygen and in air. Thus, relatively small contribution of nitrogen in air to the lower limits will be explained.

IV. UPPER LIMITS OF INFLAMMATION

For the upper limit in air a unit cell is defined as a volume per one molecule of oxygen (Fig. 3 b). In the mixture, this unit cell contains about four molecules of nitrogen and combustible molecules which may be less than one in some cases. Taking C_2 as the upper limit (volume fraction), and B as the number of combustibles in the unit cell,

$$C_2=\frac{B}{1+4+B} \tag{13}$$

or

$$B=\frac{5C_2}{1-C_2}. \tag{14}$$

If the heat of combustion per one molecule of combustibles is Q(kcal./mole) and

the activation energy is E (kcal./mole), the heat of combustion (Q_{o2}) per one molecule of oxygen is given by the relation,

$$Q_{o2}=G(Q+E)\cong GQ^{*} \tag{15}$$

where G is the number of oxygen molecules per one molecule of combustibles.

Accordingly, total degrees of freedom F is given by

$$F=5f_0+5f_BC_2/(1-C_2) \tag{16}$$

where f_0 is the degree of freedom of oxygen and nitrogen molecule, f_B that of combustibles.

If the energy Q_{o2} is given from the adjacent cell, and distributed equally among all degrees of freedom in the cell, the average energy (ε) per one degree of freedom of each molecule will be given by $(Q_{o2}/F+\frac{1}{2}RT)$. Now, it is assumed that inflammation can occur when the energy distributed for one molecule of oxygen ($f_0\varepsilon$) exceeds the activation energy E. Then the condition for inflammation may be given by the relation

$$f_0\varepsilon=f_0\left(\frac{1}{2}RT+Q_{o2}/F\right)=E. \tag{17}$$

Putting (15) and (16) into (17), we have

$$E=f_0\left\{\frac{1}{2}RT+G(Q+E)/5\left(f_0+f_B\cdot\frac{C_2}{1-C_2}\right)\right\} \tag{18}$$

Eq. (18) can be written in the from,

$$\frac{C_2}{1-C_2}=\frac{f_0}{f_B}\cdot\frac{G(Q+E)}{5\left(E-\frac{1}{2}f_0RT\right)}-1 \tag{19}$$

or

$$\frac{1}{C_2}=1+5\cdot\frac{f_B}{f_0}\cdot\frac{\left(E-\frac{1}{2}f_0RT\right)}{G(Q+E)-5\left(E-\frac{1}{2}f_0RT\right)}\cdot \tag{20}$$

In oxygen, $B=\frac{C_2}{1-C_2}$ · Accordingly Eq. (20) becomes

$$\frac{1}{C_2}=1+\frac{f_B}{f_0}\cdot\frac{E-\frac{1}{2}f_0RT}{G(Q+E)-\left(E-\frac{1}{2}f_0RT\right)}\cdot \tag{21}$$

Equations (20 and (21). mean that

* Average value of Q_{02} or approximately GQ takes almost constant value (ca. 100 kcal) for most combustibles.

(1) Upper limit (C_2) decreases with f_B, or upper limits of larger molecules are smaller than that of smaller molecules.

(2) C_2 increases with temperature, more markedly at higher temperatures.

(3) C_2 in oxygen is larger than in air.

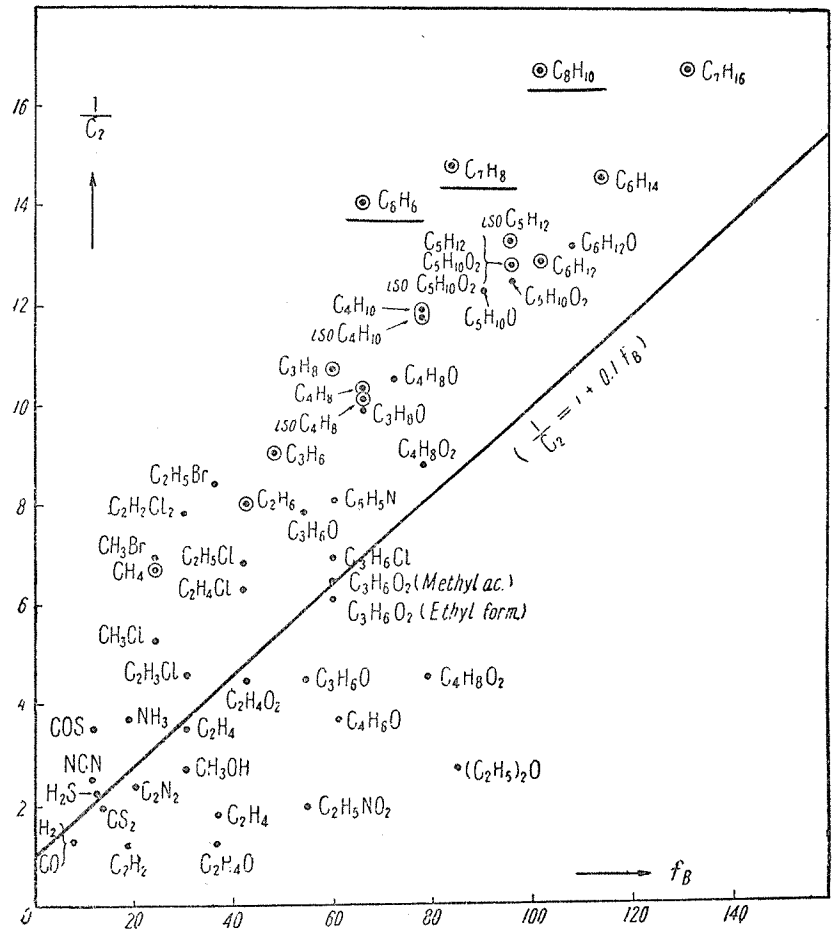


Fig. 4. Correlation between upper limit of inflamation and degrees of freedom of fuels.

These tendencies can be seen in the experimental results. Fig. 4 shows the relation of $\frac{1}{C_2}$ to f_B for various combustibles. Putting $f_0=7$, $R=0.002$ and $G(Q+E)\cong GQ\cong 100$ into Eq. (18), activation energy E can be computed as shown in Table 4. Values of activation energy in Table 4 show the same order of magnitude with those in Table 3 which have deen obtained from lower limits data.

Taking $E=12$, $T=300°K$ and $G(Q+E)\cong GQ\cong 100$ (kcal),
Eq. (21) becomes

Table 4.

Activation energy obtained upper limits data.*

Combustibles	$fB6$ (N-1)**	C_2 (%)	E (kcal)
Hydrogen	7	71.5 (20°C)	7.7
Carbon monoxide	7	70 (20°C)	8.4
Ammonia	18	25.5 (20°C)	12.6
Methane	24	13.0 (20°C)	15.4
Pentane	96	4.5 (17°C)	14.0
Benzene	66	5.3 (100°C)	16.1
Ethylene	30	13.7 (17°C)	14.0
Actylene	18	55 (17°C)	6.9
Methanol	30	25 (100°C)	16.6

Mean : $11.9 \cong 12$

$$\frac{1}{C_2} = 1 + 0.1\, f_B \qquad (22)$$

Eq. (22) is shown by a straight line in Fig. 1. It can be seen that aliphatic hydrocarbons lie on a straight line parallel to the line of Eq. (22) and aromatic hydrocarbons lie on the other line. Other compounds distribute at random. Such distribution is considered ascribable to the difference in their reaction mechanisms at the upper limits.

V. DISCUSSION

(1) Primary process of combustion and activation energy :

In this review, it has been shown that limits of inflammability and flame propagation can be discussed from a monistic point of view ; that is, a simple relation between the lower limit, upper limits, activation energy and heat of combustion can be derived from the condition for propagation which may hold for a plane flame. That relation and experimental data of inflammation limits lead to an important conclusion that the activation energy for comdustion gives an almost constant value. This conclusion suggests that the primary process is similar for most combustion, at least for hydrocarbons. The primary process of oxidation of hydrocarbons has been supposed to be as follows [11] [12] :

1. $R\,H \longrightarrow R\cdot + H$
2. $R\cdot + O_2 \longrightarrow R-O-O$

where R H is a hydrocarbon molecule and R· a radical. Especially the low temperature oxidation has been explained by thes machanisms. It is supposed that the oxidation process at the inflammation limits may be analogous to the low tempera-

* Coward and Jones : "Limits of Inflammability of Gases and Vapors" (1938).

* * N is the number of atoms in a combustible molecule (polyatomic).

ture oxidation. At the limit concentration, the heat of reaction may be equally parted between excess molecules around the combustibles and those excited molecules may contribute to the primary reaction in the adjacent zone. Further, in the presence of radicals, oxygen molecules with excess energy may induce the secand stage of the primary process (2) easily, that is, peroxidation.

(2) Equipartition law of energy :

It has been assumed that energy liberated at the flame front can be equally distributed among every degree of freedom of the reactant and excessive molecules. Strictly speaking equipartition law holds only for the system at thermal equilibrium. But results obtained above suggest that thermal equilibrium or equipartition law holds approximately in the flame front at the limits of inflammation, though it does not necessarily hold for the propagation of detonating flame containing inert gases which will be discussed elsewhere.

(3) Minimum volume and minimum energy of spark ignition :

In calculation of the temperature coefficient, unit cell has been conventionally defined as an average volume per one molecule of combustibles or oxygen. Actually it may be more reasonable to consider that the theory mentioned above holds for larger group of the unit cells. Since, in the case of spark ignition, excitation energy will be given locally and the smaller its volume, the more the dissipation of energy may be, it must have some definite volume or minimum volume in order to establish a flame.

Coward and Meitner[13] showed that minimum volume for spark ignition in methane and air mixture (8.5%) is about 1 mm^3. It is expected that there must be some close relation between this minimum volume of ignition and minimum energy for electric spark ignition which was shown by Blanc, Guest, von Elbe and Lewis[9]. They gave about 0.2 millijoule as minimum energy of spark ignition for hydrocarbons. Now, if we take 1 mm^3. as the minimum volume for ignition of methane and air mixture (8.5% for methane) number of moles of methane is $3.8 \cdot 10^{-9}$ mole.

If the minimum energy 0.2 millijoule is required to inflame the minimum volume (1 mm^3.) of 8.5% methane-air mixture, the energy E for inflammation per mole may be given as follows :

$$E = \frac{0.2}{3.8 \cdot 10^{-9}} \left(\frac{\text{millijoule}}{\text{mole}}\right) = 12.5 \left(\frac{\text{kcal}}{\text{mole}}\right).$$

Thus, it is seen that the minimum energy for spark ignition corresponds to the average activation energy for the combustible mixture estimated above by various methods.

(4) Chain mechanism and inflammation :

It has been shown in this theory that limits of inflammation or flame propagation can be discussed only from molecular stand point without any knowledge about

atomic chain mechanisms of combustion. Though we can not deny chain mechanism of combustion process, results obtained above suggest that problems about limits of inflammation or propagation may be preferably discussed in the scale of molecule or group of molecules (unit cell) instead of atomic or radical scale. Atomic or microscopic chain mechanisms may be comprised implicitly in the inflammation phenomena. In other words, the flame propagation itself may be regarded as a macroscopic chain propagation which has a definite direction of travelling.

Further, it has been shown that the assumption of equipartition law can be accepted momentarily and locally in the flame front, though, as a whole, the system never remains under thermal equilibrium during the process of combustion. It will be shown later on this Bulletin that even for propagation of detonating flame this assumption is applicable.

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